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(54) **COMPOSITION, AND METHOD FOR
PRODUCING FOAM MOLDED MATERIAL
AND ELECTRIC WIRE**

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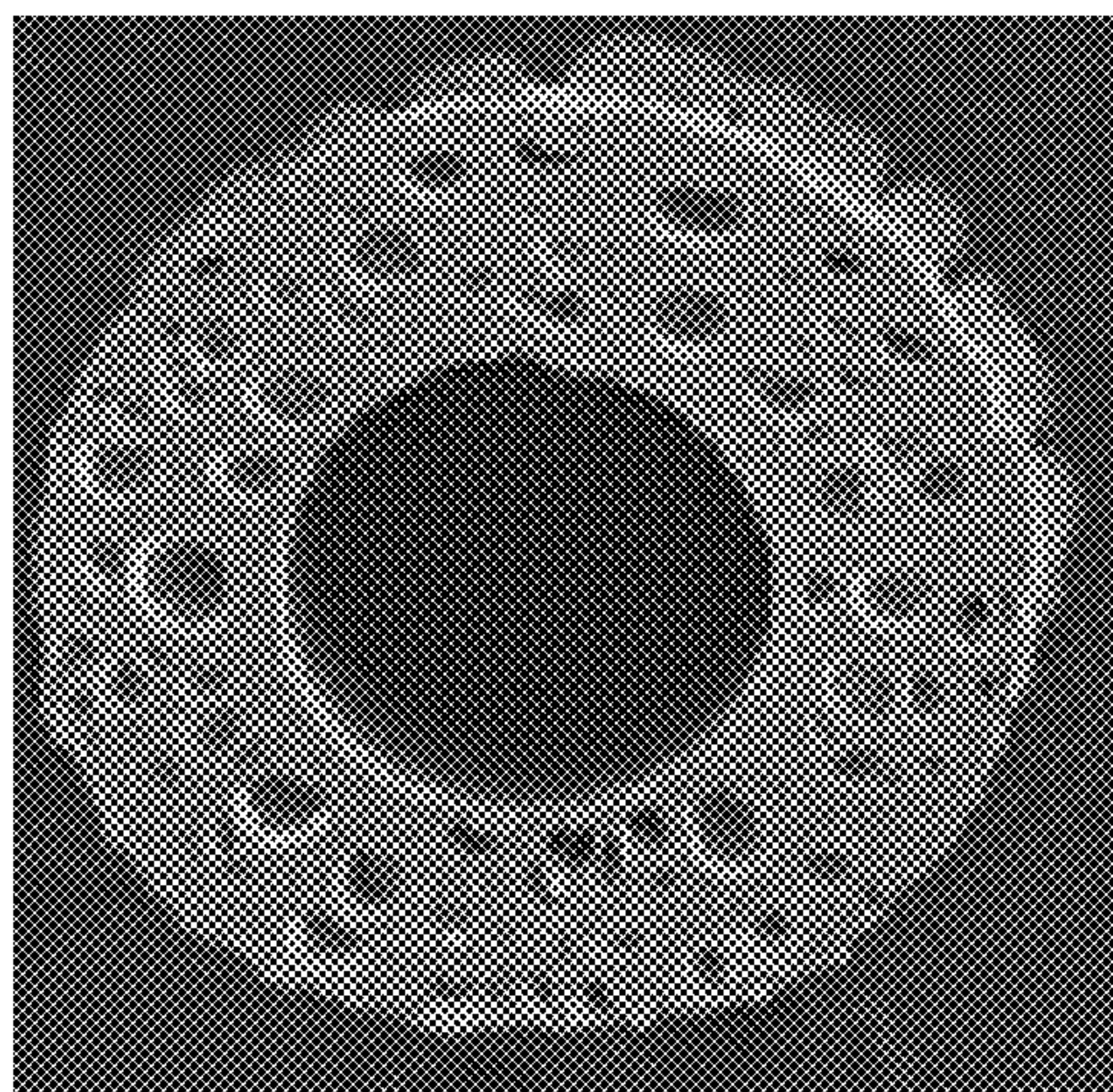
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(57) **ABSTRACT**

The present invention aims to provide a composition which
can provide molded foams and foamed electric wires having
a small average cell size and a high expansion ratio. The
composition of the present invention includes a fluororesin;
and boron nitride having an average particle size of 10.5 μm
or greater, or boron nitride having a particle size distribution
represented by (D84–D16)/D50 of 1.2 or lower.

20 Claims, 1 Drawing Sheet



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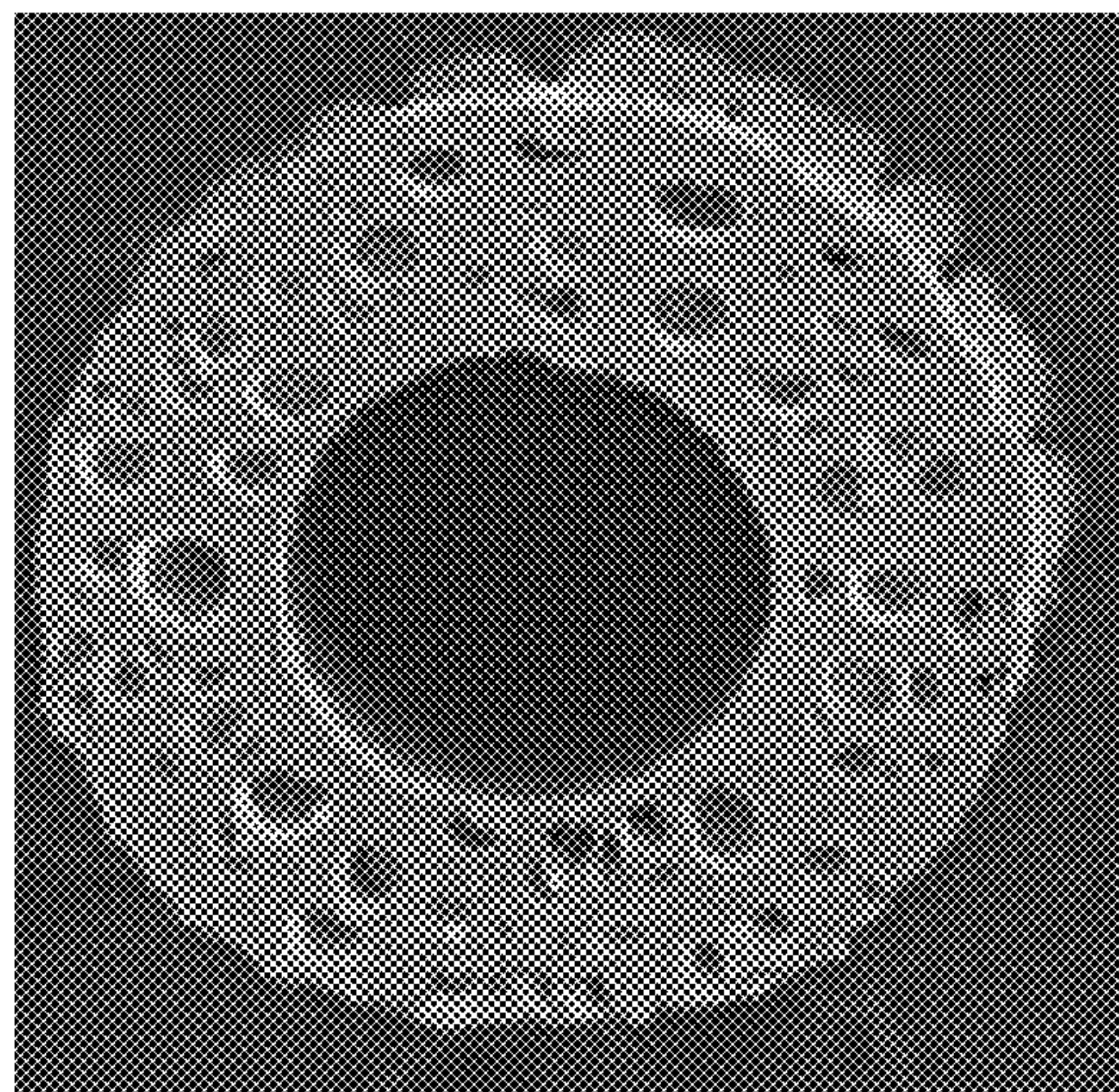
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COMPOSITION, AND METHOD FOR PRODUCING FOAM MOLDED MATERIAL AND ELECTRIC WIRE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a National Stage of International Application No. PCT/JP2014/050568 filed Jan. 15, 2014, claiming priority based on Japanese Patent Application Nos. 2013-011485, filed Jan. 24, 2013 and 2013-088770, filed Apr. 19, 2013, the contents of all of which are incorporated herein by reference in their entirety.

TECHNICAL FIELD

The present invention relates to a composition and methods for producing a molded foam and an electric wire.

BACKGROUND ART

Covering materials for electric wires are desired to have a reduced permittivity so as to improve the electrical characteristics. Such reduction in permittivity can effectively be achieved by using foams as covering materials. Foams made of resin material can usually be produced by a foam-molding process in which gas is introduced into a molten resin and then molded.

In order to equalize the shape and the properties of the resulting foam, the cells in the foam are preferably fine and uniformly distributed therein. For the purpose of making the cells fine and of distributing the cells uniformly, a foam nucleating agent, which is to serve as the starting point of generating cells during the foam molding, may be introduced into a resin.

One typical example of the foam nucleating agent added to resin such as fluoro-resin is boron nitride (BN) because BN has thermal stability, chemical inertness, low toxicity, and excellent electric properties (for example, it causes only a slight change in permittivity when added).

The following disclosures provide examples of a method of producing a foam by mixing BN as a foam nucleating agent to resin such as fluoro-resin.

Patent Literature 1 discloses that a foam nucleating agent is preferably a combination of BN with zeolite among combinations of any of ceramics and materials thereof with zeolite.

Patent Literature documents 2 and 3 disclose a method in which BN is used as a foam nucleating agent.

Patent Literature 3 also discloses a method in which BN having a surface area of 5 to 10 m²/g is added as a foam nucleating agent.

Patent Literature documents 4, 5, and 6 disclose combination use of boron nitride having a surface area of 8.6 m²/g with any of sulfonic acids, phosphonic acids, and salts thereof.

Patent Literature documents 7 and 8 disclose combination use of BN having a surface area of about 8 m²/g with any thermally stable inorganic salt which comprises metal cations and polyatomic anions and which satisfies a specific formula, such as sodium tetraborate.

Patent Literature 9 discloses that BN used in the formation of fluoro-resin foams preferably has an average particle size of smaller than 10 μm and a resin and the BN are pulverized using an appropriate mill.

Patent Literature 10 discloses a method in which a resin powder foamable by decarboxylation, BN, and a metal salt

are mixed to provide a blend, and next the blend is coarsely pulverized into a pulverized powder using a compressor and then a grinder such as a hammer mill, or the blend is formed into pellets using a pellet mill, and thereafter the powder or the pellets are fed into an extruder. The literature discloses that the mixing is preferably performed with a HENSCHEL mixer (Purnell International).

Patent Literature 11 discloses a foaming method in which a processible fluoropolymer material and BN, as well as a sulfonic acid, a phosphonic acid, or a salt thereof, and/or a polyatomic anion-containing inorganic salt are used together, wherein the BN crystals are grown to the final size and have an average particle size of 12 μm or smaller. The literature discloses that, when the respective grown crystallites agglomerate, the BN crystals are prepared not by mechanical pulverization, in which the respective crystals are pulverized, but by deagglomeration.

Patent Literature 12 discloses a resin composition containing a fluoro-resin (A) and a foam nucleating agent (B), wherein the foam nucleating agent (B) has a d₉₉ value of 15 μm or smaller. Boron nitride is used as the foam nucleating agent (B).

Patent Literature 13 discloses a composition containing a specific fluorine-containing copolymer suited for use in the fabrication of foamed articles. The literature also discloses that the composition may contain boron nitride. Patent Literature documents 14 and 15 disclose a fluorine-containing polymer which has a high melt flow rate and which is capable of being extruded at high speed, and also disclose boron nitride as a foam nucleating agent to be added to the fluorine-containing polymer.

Patent Literature documents 16 and 17 disclose a fluoro-resin composition comprising 100 parts by mass of a tetrafluoroethylene/hexafluoropropylene copolymer and 0.01 to 3 parts by mass of polytetrafluoroethylene having a standard specific gravity of 2.15 to 2.30, wherein the fluoro-resin composition is obtainable by mixing an aqueous dispersion of the tetrafluoroethylene/hexafluoropropylene copolymer and an aqueous dispersion of the polytetrafluoroethylene, coagulating the dispersed matter, and then drying the coagulum and melt-extruding the dried matter. The documents also disclose that a foamed electric wire is produced from the composition containing boron nitride.

CITATION LIST

Patent Literature

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SUMMARY OF INVENTION

Technical Problem

In consideration of the aforementioned situation, the present invention aims to provide a composition capable of

providing molded foams and foamed electric wires that have a small average cell size and a high expansion ratio.

Solution to Problem

The present invention relates to a composition comprising a fluoro-resin and boron nitride having an average particle size of 10.5 μm or greater (hereinafter, also referred to as a “first composition”).

In the first composition of the present invention, the boron nitride preferably has a particle size distribution represented by (D84–D16)/D50 of 1.2 or lower.

The present invention also relates to a composition comprising a fluoro-resin and boron nitride having a particle size distribution represented by (D84–D16)/D50 of 1.2 or lower (hereinafter, also referred to as a “second composition”).

In the second composition of the present invention, the boron nitride preferably has an average particle size of 5.0 μm or greater.

In the first and second compositions of the present invention, the boron nitride is preferably in a pulverized form.

The fluoro-resin in each of the first and second compositions of the present invention is preferably a tetrafluoroethylene/hexafluoropropylene copolymer, a tetrafluoroethylene/perfluoro(alkyl vinyl ether) copolymer, or a tetrafluoroethylene/ethylene copolymer.

The fluoro-resin in each of the first and second compositions of the present invention is preferably, but not limited to, a fluorinated fluoro-resin.

In each of the first and second compositions of the present invention, the amount of the boron nitride is preferably 0.5% by mass or more based on the sum of the amounts of the fluoro-resin and the boron nitride.

The first and second compositions of the present invention each preferably further comprise a sulfonic acid or a salt thereof.

The sulfonic acid or a salt thereof is preferably a sulfonic acid represented by the following formula (1):



wherein n is 4 or 5; or the following formula (2):



wherein n is 4 or 5, or a salt thereof.

The present invention also relates to a molded foam which is formed from any of the above compositions.

The present invention also relates to an electric wire comprising a core and a covering material which covers the core and which is formed from any of the above compositions.

The present invention also relates to a method for producing a molded foam, comprising foam-molding any of the above compositions.

The present invention also relates to a method for producing an electric wire, comprising covering a core with any of the above compositions to provide an electric wire.

Advantageous Effects of Invention

Since the compositions of the present invention have the aforementioned structure, they can provide molded foams and foamed electric wires which have a small average cell size and a high expansion ratio.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photograph showing the cross section of an electric wire produced in Example 10.

DESCRIPTION OF EMBODIMENTS

The first composition of the present invention comprises a fluoro-resin and boron nitride having an average particle size of 10.5 μm or greater.

The second composition of the present invention comprises a fluoro-resin and boron nitride having a particle size distribution represented by (D84–D16)/D50 of 1.2 or lower.

The following will describe the present invention in detail.

The boron nitride in the first composition of the present invention has an average particle size of 10.5 μm or greater. The technicians tend to make the average particle size of boron nitride small and never specifically examined the use of boron nitride having a relatively large average particle size.

However, the first composition of the present invention containing boron nitride having an average particle size within the above specific range can provide molded foams and foamed electric wires having a small average cell size and a high expansion ratio. An average cell size of smaller than 10.5 μm leads to a large average cell size. Such an average cell size also leads to a low expansion ratio.

The average particle size of the boron nitride in the first composition of the present invention is more preferably 11.0 μm or greater, still more preferably 12.0 μm or greater, much more preferably 13.0 μm or greater, and particularly preferably 15.0 μm or greater. Boron nitride having an average particle size within the above range can provide molded foams and foamed electric wires having a small average cell size and a high expansion ratio.

Boron nitride having too large an average particle size may cause the occurrence of many sparks. The average particle size of the boron nitride is preferably 25.0 μm or smaller, and more preferably 20.0 μm or smaller.

The average particle size of the boron nitride is a value determined using a laser diffraction scattering particle size distribution analyzer (e.g., Microtrac MT3300, NIKKISO CO., LTD.). In the case of a wet process, any appropriately selected medium such as methanol can be used.

The boron nitride in the first composition of the present invention preferably has a particle size distribution (D84–D16)/D50 of 1.2 or lower.

When a cumulative curve is drawn with the whole volume of the group of the boron nitride powder taken as 100%, the above D84, D50, and D16 represent the particle size (μm) at the point where the curve reaches 84%, the particle size (μm) at the point where the curve reaches 50%, and the particle size (μm) at the point where the curve reaches 16%, respectively. The accumulation of the particle size distribution starts from the smallest particle size. The whole volume of the group of the powder can be determined on a sample prepared by dispersing the boron nitride powder in a medium such as methanol using a laser diffraction scattering particle size distribution analyzer (e.g., Microtrac MT3300, NIKKISO CO., LTD.).

The boron nitride having a particle size distribution within the above range enables production of covering materials having fine, uniform cells and more suppression of the occurrence of sparks.

The particle size distribution is more preferably 1.1 or lower, and still more preferably 1.0 or lower. The lower limit of the particle size distribution is not particularly limited, and it may be 0.1, for example.

The cumulative curve of the particle size distribution (volume-based particle size distribution) can be obtained using a laser diffraction scattering particle size distribution

analyzer (e.g., Microtrac MT3300, NIKKISO CO., LTD.). In the case of a wet process, any appropriate medium such as methanol can be used.

The boron nitride in the second composition of the present invention has a particle size distribution (D84–D16)/D50 of 1.2 or lower.

The technicians have examined to make the average particle size of boron nitride small, but never specifically performed examinations focusing on the particle size distribution of boron nitride.

Since the second composition of the present invention comprises boron nitride having an average particle size within the above specific range, it can provide molded foams and foamed electric wires having a small average cell size and a high expansion ratio.

When a cumulative curve is drawn with the whole volume of the group of the boron nitride powder taken as 100%, the above D84, D50, and D16 represent the particle size (μm) at the point where the curve reaches 84%, the particle size (μm) at the point where the curve reaches 50%, and the particle size (μm) at the point where the curve reaches 16%, respectively. The accumulation of the particle size distribution starts from the smallest particle size. The whole volume of the group of the powder can be determined on a sample prepared by dispersing the boron nitride powder in a medium such as methanol using a laser diffraction scattering particle size distribution analyzer (e.g., Microtrac MT3300, NIKKISO CO., LTD.).

The boron nitride having a particle size distribution within the above range enables production of covering materials having fine, uniform cells and more suppression of the occurrence of sparks.

The particle size distribution is preferably 1.1 or lower, and more preferably 1.0 or lower. The lower limit of the particle size distribution may be, but not limited to, 0.1, for example.

The cumulative curve of the particle size distribution (volume particle size distribution) can be determined using a laser diffraction scattering particle size distribution analyzer. In the case of a wet process, the medium can be methanol.

The boron nitride in the second composition of the present invention preferably has an average particle size of 5.0 μm or greater. The average particle size is more preferably 8.0 μm or greater, still more preferably 8.5 μm or greater, and much more preferably 10.5 μm or greater. The boron nitride having an average particle size within the above range enables production of molded foams and foamed electric wires having a smaller average cell size and a higher expansion ratio. The average particle size of the boron nitride is preferably 25.0 μm or smaller, and more preferably 20.0 μm or smaller. The average particle size of the boron nitride may be smaller than 10.5 μm .

The average particle size of the boron nitride is a value determined using a laser diffraction scattering particle size distribution analyzer (e.g., Microtrac MT3300, NIKKISO CO., LTD.). In the case of a wet process, any appropriate medium such as methanol can be used.

The boron nitride in each of the first and second compositions of the present invention is preferably in a pulverized form. Such pulverized boron nitride enables production of molded foams and foamed electric wires having a small average cell size and a high expansion ratio. Also, it enables production of molded foams and foamed electric wires causing less sparks.

The pulverization can be performed by a method and under conditions in which the boron nitride is allowed to

have an average particle size and a particle size distribution within the above respective ranges. For example, the type and the conditions of a pulverizer are appropriately adjusted. Examples of the pulverizer include a jet mill, a hammer mill, a ball mill, and a pin mill.

The average particle size and particle size distribution of the boron nitride can be adjusted to fall within the above respective ranges by classification.

In the first and second compositions of the present invention, the amount of the boron nitride based on the sum of the amounts of the fluoro resin and the boron nitride is preferably 0.1% by mass or more, more preferably 0.4% by mass or more, still more preferably 0.5% by mass, and much more preferably 0.6% by mass or more. Too small an amount of the boron nitride tends to cause a failure in giving fine cells to the resulting covering material for foamed electric wires.

The amount of the boron nitride based on the sum of the amounts of the fluoro resin and the boron nitride is particularly preferably 0.7% by mass or more. Boron nitride in an amount of 0.7% by mass or more enables production of molded foams and foamed electric wires particularly excellent in a balance between the average cell size and the expansion ratio.

The amount of the boron nitride based on the sum of the amounts of the fluoro resin and the boron nitride is preferably 2.0% by mass or less, more preferably 1.5% by mass or less, and still more preferably 1.0% by mass or less. Too large an amount of the boron nitride may cause a high production cost.

The fluoro resin in each of the first and second compositions of the present invention may be any melt-processible one. Examples thereof include tetrafluoroethylene (TFE)/hexafluoropropylene (HFP) copolymers, TFE/perfluoro(alkyl vinyl ether) (PAVE) copolymers, TFE/ethylene copolymers (ETFE), chlorotrifluoroethylene (CTFE)/ethylene copolymers (ECTFE), polyvinylidene fluoride (PVdF), polychlorotrifluoroethylene (PCTFE), TFE/vinylidene fluoride (VdF) copolymers (VT), polyvinyl fluoride (PVF), TFE/VdF/CTFE copolymers (VTC), TFE/ethylene/HFP copolymers, and TFE/HFP/VdF copolymers.

Examples of the PAVE include perfluoro(methyl vinyl ether) (PMVE), perfluoro(ethyl vinyl ether) (PEVE), and perfluoro(propyl vinyl ether) (PPVE). PPVE is preferred. One of them may be used alone or two or more of them may be used in combination.

The fluoro resin may have an additional polymer unit derived from another monomer in an amount that causes no deterioration in the essential properties of the respective fluoro resins. Such an additional monomer can appropriately be selected from TFE, HFP, ethylene, propylene, perfluoro(alkyl vinyl ethers), perfluoroalkylethylenes, hydrofluoroolefins, fluoroalkylethylenes, perfluoro(alkyl allyl ethers), and the like. The perfluoroalkyl group in the additional monomer preferably has 1 to 10 carbon atoms.

Because of their excellent heat resistance, the fluoro resin is preferably selected from TFE/HFP copolymers, TFE/PAVE copolymers, and TFE/ethylene copolymers, and more preferably selected from TFE/HFP copolymers and TFE/PAVE copolymers. Two or more of these fluoro resins may be used in combination. Because of its more excellent electrical properties, the fluoro resin is also preferably a perfluoro resin.

The TFE/HFP copolymer preferably satisfies a TFE/HFP mass ratio of 80 to 97/3 to 20, and more preferably 84 to 92/8 to 16.

The TFE/HFP copolymer may be a copolymer consisting of TFE and HFP, or may be a terpolymer consisting of TFE,

HFP, and a comonomer copolymerizable with TFE and HFP (e.g., a TFE/HFP/PAVE copolymer).

The TFE/HFP copolymer is also preferably a TFE/HFP/PAVE copolymer including a polymer unit derived from PAVE.

The TFE/HFP/PAVE copolymer preferably satisfies a TFE/HFP/PAVE mass ratio of 70 to 97/3 to 20/0.1 to 10, and more preferably 81 to 92/5 to 16/0.3 to 5.

The TFE/PAVE copolymer preferably satisfies a TFE/PAVE mass ratio of 90 to 99/1 to 10, and more preferably 92 to 97/3 to 8.

The TFE/ethylene copolymer preferably satisfies a TFE/ethylene mole ratio of 20 to 80/20 to 80, and more preferably 40 to 65/35 to 60. The TFE/ethylene copolymer may include another monomer component.

In other words, the TFE/ethylene copolymer may be a copolymer consisting of TFE and ethylene, or may be a terpolymer consisting of TFE, ethylene, and a comonomer copolymerizable with TFE and ethylene (e.g., a TFE/ethylene/HFP copolymer).

The TFE/ethylene copolymer may also preferably be a TFE/ethylene/HFP copolymer including a polymer unit derived from HFP. The TFE/ethylene/HFP copolymer preferably satisfies a TFE/ethylene/HFP mole ratio of 40 to 65/30 to 60/0.5 to 20, and more preferably 40 to 65/30 to 60/0.5 to 10.

The fluororesin preferably has a melt flow rate (MFR) of 0.1 to 100 g/10 min. The MFR is more preferably 4 to 70 g/10 min, and still more preferably 19 to 60 g/10 min. In order to suppress the occurrence of sparks and increase the expansion ratio, the MFR is much more preferably 34 to 50 g/10 min, and particularly preferably 34 to 42 g/10 min. The MFR is a value determined in conformity with ASTM D1238 using a die having a diameter of 2.1 mm and a length of 8 mm at a load of 5 kg and a temperature of 372° C.

The fluororesin can be synthesized by polymerizing monomer components through a usual polymerization method, such as emulsion polymerization, suspension polymerization, solution polymerization, bulk polymerization, or gas phase polymerization. In the polymerization reaction, a chain-transfer agent such as methanol may be used in some cases. The fluororesin may be produced by polymerization and isolation without using a metal-ion-containing reagent.

The fluororesin may have an end group such as —CF₃ or —CF₂H on at least one of the polymer main and side chains. Although not limited to, the fluororesin is preferably a fluorinated fluororesin. Non-fluorinated fluororesins may have a thermally and electrically unstable end group (hereinafter, such an end group is also referred to as an “unstable end group”) such as —COOH, —CH₂OH, —COF, and —CONH₂. These unstable end groups can be reduced by fluorination.

The fluororesin preferably includes a small number of unstable end groups or no such groups. More preferably, the total number of the above-exemplified four species of unstable end groups and —CF₂H end groups is 50 or less per 1×10⁶ carbon atoms. More than 50 unstable end groups may cause molding defects. The number of unstable end groups is more preferably 20 or less, and still more preferably 10 or less. The number of unstable end groups herein is a value determined by infrared absorption spectrometry. The fluororesin may have neither unstable end groups nor —CF₂H end groups, and all the end groups therein may be —CF₃ end groups.

The fluorination can be achieved by bringing a non-fluorinated fluororesin into contact with a fluorine-containing compound.

The fluorine-containing compound may be any such compound, and examples thereof include fluorine radical sources that generate fluorine radicals under the fluorination conditions. Examples of the fluorine radical source include F₂ gas, CoF₃, AgF₂, UF₆, OF₂, N₂F₂, CF₃OF, and halogen fluorides (e.g., IF₅, ClF₃).

The concentration of the fluorine radical source such as F₂ gas may be 100%. In order to ensure the safety, the fluorine radical source is preferably diluted with an inert gas to 5 to 50% by mass, and preferably 15 to 30% by mass. Examples of the inert gas include nitrogen gas, helium gas, and argon gas. In order to save the cost, nitrogen gas is preferred.

The fluorination can be performed under any conditions. A molten fluororesin may be brought into contact with a fluorine-containing compound. Still, the fluorination is usually performed at a temperature of not higher than the melting point of the fluororesin, preferably 20° C. to 220° C., and more preferably 100° C. to 200° C. The fluorination is usually performed for 1 to 30 hours, and preferably 5 to 20 hours.

The fluorination is preferably achieved by bringing a non-fluorinated fluororesin with a fluorine gas (F₂ gas).

The first and second compositions of the present invention each may further comprise a polyatomic anion-containing inorganic salt and a sulfonic acid, a phosphonic acid, or a salt thereof.

Examples of the polyatomic anion-containing inorganic salt include those disclosed in U.S. Pat. No. 4,764,538 A.

The first and second compositions of the present invention each preferably further comprise a sulfonic acid or a salt thereof in addition to the fluororesin and the boron nitride having an average particle size of 10.5 μm or greater or the boron nitride having a particle size distribution represented by (D84–D16)/D50 of 1.2 or lower.

The sulfonic acid or a salt thereof is preferably an alkali metal salt or an alkaline earth metal salt because of their excellent heat resistance.

The sulfonic acid or a salt thereof is preferably a compound (A) which is a sulfonic acid represented by the following formula (1):



wherein n is 4 or 5, or the following formula (2):



wherein n is 4 or 5, or a salt thereof.

Use of the compound (A) enables production of molded foams and foamed electric wires having a small average cell size and a high expansion ratio.

In order to give a good balance between the average cell size and the expansion ratio to the resulting covering materials formed from the first and second compositions of the present invention, the compound (A) is preferably a sulfonic acid represented by the formula (1) or (2), or an alkali metal salt or an alkaline earth metal salt thereof. The compound (A) is more preferably a barium salt, a potassium salt, a sodium salt, or a rubidium salt of a sulfonic acid represented by the formula (1) or (2).

In each of the first and second compositions of the present invention, the amount of the compound (A) is preferably 2000 ppm or less, and more preferably 1500 ppm or less, based on the amount of the fluororesin. It is still more preferably 1000 ppm or less, much more preferably 500 ppm or less, and particularly preferably 250 ppm or less.

In the compositions of the present invention, the amount of the compound (A) is preferably 0.01 ppm or more based on the amount of the fluororesin. It is more preferably 0.1 ppm or more.

Too small an amount of the compound (A) may cause the resulting covering materials to have less fine cells. Too large an amount thereof may cause the occurrence of many sparks.

In the case of using a barium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 1500 ppm or less based on the amount of the fluororesin. It is more preferably 1000 ppm or less, and still more preferably 500 ppm or less.

In the case of using a barium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 0.01 ppm or more based on the amount of the fluororesin. It is more preferably 0.1 ppm or more, still more preferably 1 ppm or more, much more preferably 4 ppm or more, and particularly preferably 10 ppm or more.

Too small an amount of the compound (A) may lead to a failure in forming fine cells. Too large an amount thereof may cause the occurrence of many sparks.

In the case of using a potassium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 2000 ppm or less based on the amount of the fluororesin. It is more preferably 1500 ppm or less, still more preferably 1000 ppm or less, and particularly preferably 500 ppm or less.

In the case of using a potassium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 0.01 ppm or more based on the amount of the fluororesin. It is more preferably 0.1 ppm or more, still more preferably 1 ppm or more, much more preferably 4 ppm or more, and particularly preferably 10 ppm or more.

Too small an amount of the compound (A) may lead to a failure in forming fine cells. Too large an amount thereof may cause the occurrence of many sparks.

The compound (A) is preferably a sodium salt. In the case of using a sodium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 250 ppm or less based on the amount of the fluororesin. It is more preferably 100 ppm or less.

In the case of using a sodium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 0.01 ppm or more based on the amount of the fluororesin. It is more preferably 0.1 ppm or more, still more preferably 1 ppm or more, much more preferably 4 ppm or more, and particularly preferably 10 ppm or more.

Too small an amount of the compound (A) may lead to a failure in forming fine cells. Too large an amount thereof may cause the occurrence of many sparks.

The compound (A) is preferably a rubidium salt because this salt makes it very easy to control the expansion ratio. In the case of using a rubidium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 500 ppm or less based on the amount of the fluororesin. It is more preferably 250 ppm or less.

In the case of using a rubidium salt as the compound (A) in the compositions of the present invention, the amount of the compound (A) is preferably 0.01 ppm or more based on the amount of the fluororesin. It is more preferably 0.1 ppm or more, still more preferably 1 ppm or more, much more preferably 4 ppm or more, and particularly preferably 10 ppm or more.

Too small an amount of the compound (A) may lead to a failure in forming fine cells. Too large an amount thereof may cause the occurrence of many sparks.

In general, C—F bonds have a higher binding energy and a chemically stronger structure than C—H bonds. Thus, the compound (A) is more preferably a sulfonic acid of the formula (1) or a salt thereof having no C—H bond.

The first and second compositions of the present invention each may comprise, in addition to the fluororesin and the boron nitride, conventionally known filler in an amount that does not deteriorate the effects of the present invention.

Examples of the filler include graphite, carbon fiber, coke, silica, zinc oxide, magnesium oxide, tin oxide, antimony oxide, calcium carbonate, magnesium carbonate, glass, talc, mica, mica, aluminum nitride, calcium phosphate, sericite, diatomite, silicon nitride, fine silica, alumina, zirconia, quartz powder, kaolin, bentonite, and titanium oxide. The filler may be in any form. For examples, the filler may be in the form of fibers, needles, powder, particles, beads, or the like. The filler is different from the boron nitride.

The first and second compositions of the present invention each may further comprise a thermoplastic resin that is different from the aforementioned fluororesin. Examples of the thermoplastic resin different from the aforementioned fluororesin include general-purpose resins such as polyethylene resin, polypropylene resin, vinyl chloride resin, and polystyrene resin; and engineering plastics such as nylon, polycarbonate, polyether ether ketone resin, and polyphenylene sulfide resin.

The first and second compositions of the present invention each may further comprise any of other components such as additives. Examples of such components include fillers such as glass fiber, glass powder, and asbestos fiber, reinforcing agents, stabilizers, lubricants, pigments, and other additives.

The first or second composition of the present invention can be produced by, for example, a production method including mixing the fluororesin and boron nitride having an average particle size of 10.5 μm or greater or boron nitride having a particle size distribution represented by (D84—D16)/D50 of 1.2 or lower (hereinafter, also referred to as a “method for producing a composition”).

The mixing method may be any conventionally known method. Preferred is a mixing method in which the boron nitride is less likely to coagulate.

The mixing method may be one using a Henschel mixer, a ribbon mixer, a V blender, a ball mill, or the like. A mixing method utilizing melt-kneading may be used.

The above production method for the composition may include pulverizing and/or classifying boron nitride to provide boron nitride having an average particle size of 10.5 μm or greater or boron nitride having a particle size distribution represented by (D84—D16)/D50 of 1.2 or lower before the above mixing.

The production method for the above composition may include kneading the mixture prepared in the above mixing. The kneading provides pellets. The kneading can be performed by a method using a conventionally known melt-kneading device such as a single screw extruder or a twin screw extruder.

The method for producing the above composition may include fluorinating the fluororesin. The fluorination can be performed by any of the aforementioned methods. For example, the fluorination may be performed by bringing the pellets prepared by the above kneading into contact with the aforementioned fluorine-containing compound.

The above described components that may be contained in each of the compositions of the present invention, such as

thermoplastic resins excluding the fluororesin, polyatomic anion-containing inorganic salts, sulfonic acids, phosphonic acids, and salts thereof, fillers, and other additives, can appropriately be added in any of the steps of the method for producing the composition in accordance with the properties and the like factors of the components. The fluororesin and the boron nitride may further be added.

The compositions of the present invention each can suitably be used as a foamable composition. The composition can also suitably be used as a composition for molded foams. The compositions each can further be suitably used as a composition for forming covering materials of electric wires.

The method for producing a molded foam of the present invention includes foam-molding the aforementioned first or second composition.

The composition can be foam-molded by any method, including conventionally known methods. For example, the fluororesin of the present invention in the molten state (molten resin) is charged together with a gas into a screw extruder designed for foaming operations, and then a continuous gas injection method is performed.

Examples of the gas include gases of chlorodifluoromethane, nitrogen, and carbon dioxide, and any mixtures of these gases. The gas in the form of a pressurized gas may be introduced into the molten resin in the extruder, or the gas may be generated by mingling a chemical foaming agent into the molten resin. The gas dissolves in the molten resin in the extruder.

When the molten material is extruded through an extrusion die, the gas dissolved in the molten resin emerges from the molten material in response to this sudden pressure decrease. The material extruded through the extruder is then, for example, put into water to be cooled down and solidified.

Since the molded foam is a product of foam-molding the composition, it has a low permittivity, a stable capacitance, and a light weight, and it can particularly provide a covering material to be mentioned later having stable dimensions such as the wire diameter and the thickness.

The total volume of the cells in the molded foam can appropriately be adjusted so as to fit the use thereof by, for example, adjusting the amount of gas introduced into the extruder or selecting the type of gas to be dissolved.

The molded foam can be produced as a molded material molded through the extruder so as to have a shape that fits the use thereof. The molding method can be any heat melt molding, and examples thereof include extrusion foam molding, injection foam molding, and mold foam molding.

The molded foam can have any shape. For example, it can be formed into any of various shapes, including the covering materials such as foamed electric wires; filament-like shapes such as the shapes of wire rods; sheet-like shapes; film-like shapes; rod-like shapes; and pipe-like shapes. Examples of the use of the molded foam include electrical insulating materials; heat insulating materials; sound insulating materials; light-weight structural materials such as floating materials; and cushioning materials such as cushions. The molded foam can particularly suitably be used as a covering material for foamed electric wires.

Preferably, the resulting molded foam contains a melt-solidified matter of the composition of the present invention and cells, and the cells are uniformly distributed in the melt-solidified matter. The cells may have any average cell size, and it is preferably 60 μm or smaller, for example. The average cell size is also preferably 0.1 μm or greater.

The molded foam may have any expansion ratio, and the ratio is preferably 20% or higher. The upper limit of the expansion ratio may be, although not limited to, 80%.

The method for producing an electric wire of the present invention includes covering a core with the composition to provide an electric wire. The use of the composition enables to form a foamed electric wire comprising a covering material that includes fine, uniform cells. The production of an electric wire preferably includes foam-molding the composition.

The electric wire produced by the method for producing an electric wire comprises a core and a covering material formed from the composition. An electric wire comprising a core covered with the composition is also one aspect of the present invention.

Since the covering material comprises a core covered with the composition, it includes fine, uniform cells. Further, the covering material can have a low permittivity, a stable capacitance, a light weight, and a shape having stable dimensions such as the diameter and the thickness.

The electric wire can be produced by a conventionally known method except that the core is covered with the aforementioned composition. For example, the electric wire can be produced by extrusion foam molding. Preferable conditions for extrusion molding can appropriately be selected in accordance with the components of the composition and the size of the core.

Examples of a method of covering the core with the composition include a method in which a molten fluororesin (molten resin) is used with a gas so that the composition of the present invention is charged into a screw extruder designed for foaming operations, performing a continuous gas injection method. The gas may be the same gas as used in the method for producing a molded foam.

Preferably, the resulting covering material comprises a melt-solidified matter of the composition of the present invention and cells, and the cells are uniformly distributed in the melt-solidified matter.

The cells may have any average cell size. For example, the average cell size is preferably 60 μm or smaller, more preferably 45 μm or smaller, still more preferably 35 μm or smaller, much more preferably 30 μm or smaller, particularly preferably 25 μm or smaller, and more particularly preferably 23 μm or smaller. Combination use of the boron nitride and the sulfonic acid or a salt thereof represented by the formula (1) or (2) makes it possible to adjust the average cell size of cells to 23 μm or smaller more easily.

The average cell size is also preferably 0.1 μm or greater, and more preferably 1 μm or greater.

Such a structure of the covering material is attributed to the specific average particle size of the boron nitride in the composition of the present invention.

The average cell size is a value determined as follows: taking an image of the cross section of the covering material by a scanning electron microscope (SEM); processing the image and calculating the diameters of the respective cells; and calculating the average value thereof.

The covering material preferably has an expansion ratio of 20% or higher. It is more preferably 30% or higher, still more preferably 33% or higher, and much more preferably 35% or higher. The upper limit thereof may be, although not limited to, 80%. The upper limit of the expansion ratio may be 60%.

The expansion ratio is a value determined by $\left[\frac{\text{(specific gravity of fluororesin)} - \text{(specific gravity of foam)}}{\text{(specific gravity of fluororesin)}}\right] \times 100$. The expansion ratio can appropriately be adjusted so as to suit the use thereof by, for

example, adjusting the amount of gas to be introduced into the extruder or selecting the type of gas to be dissolved.

The covering material preferably causes less than five sparks per 3500 m. It more preferably causes less than three sparks, and still more preferably not more than one spark.

The number of sparks is a value determined by measurement at a voltage of 1500 V using a spark tester HFS1220 (Beta LaserMike).

The material of the core may be a conductive metal material such as copper or aluminum, for example. The core is preferably 0.02 to 3 mm in diameter. The diameter of the core is more preferably 0.04 mm or greater, still more preferably 0.05 mm or greater, and particularly preferably 0.1 mm or greater. The diameter of the core is more preferably 2 mm or smaller.

The covering material of the electric wire is preferably 0.1 to 3.0 mm in thickness. The thickness of the covering material is also preferably 2.0 mm or smaller.

Specific examples of the core include those satisfying AWG-46 (40- μ m-diameter solid copper wires), those satisfying AWG-26 (404- μ m-diameter solid copper wires), those satisfying AWG-24 (510- μ m-diameter solid copper wires), and those satisfying AWG-22 (635- μ m-diameter solid copper wires); here, AWG represents the American wire gauge.

The foamed electric wire comprises a core and a covering material that covers the core. Examples of the use of the foamed electric wire include cables for connecting computers and peripherals, such as cables for LAN.

The foamed electric wire may have a double-layered (skin-foam) structure comprising a core, a covering material, and a non-foam layer disposed therebetween, a double-layered (foam-skin) structure comprising a non-foam layer that covers the peripheral layer of the wire, or a triple-layered (skin-foam-skin) structure comprising a non-foam layer that covers the peripheral layer of the skin-foam structure.

The non-foam layer of the electric wire may be any resin layer formed of a resin such as any of TFE/HFP copolymers, TFE/PAVE copolymers, TFE/ethylene copolymers, vinylidene fluoride polymers, polyolefin resins (e.g., polyethylene (PE)), and polyvinyl chloride (PVC).

EXAMPLES

The present invention is described in detail below referring to, but not limited to, examples.

The properties herein were determined by the following methods.

(Average Particle Size and Particle Size Distribution of Boron Nitride)

About 30 mg of boron nitride powder was put into about 20 ml of methanol and dispersed therein for two minutes using an ultrasonic cleaner (electric power: 100 W). Then, the parameters were determined using Microtrac MT3300 (NIKKISO CO., LTD.) by a wet process (transmission, particle refractive index: 1.63). The average particle size and the particle size distribution were each determined twice, and the average values of the respective parameters were determined.

The particle size distribution was determined as follows. A cumulative curve was drawn with the whole volume of the group of boron nitride powder taken as 100%. The D84, D50, and D16 values were calculated from the cumulative curve, and the value represented by (D84-D16)/D50 was used as the standard of the particle size distribution. The D84, D50, and D16 values represent the particle size (μ m) at the point where the curve reaches 84%, the particle size

(μ m) at the point where the curve reaches 50%, and the particle size (μ m) at the point where the curve reaches 16%, respectively. The accumulation of the particle size distribution started from the smallest particle size.

This method of measuring the particle size distribution is a usual method and the D50 value, which is a cumulative average value (median diameter), is one of the usual parameters for evaluating the particle size distribution. (Melting Point)

The melting point of the fluororesin was a temperature corresponding to the peak in the measurement using RDC220 (Seiko Instruments Inc.) at a temperature-increasing rate of 10° C./min.

(MFR)

The MFR of the fluororesin was a value determined in conformity with ASTM D1238 using a KAYENESS Series 4000 melt indexer (YASUDA SEIKI SEISAKUSHO, LTD.) and a die having a diameter of 2.1 mm and a length of 8 mm at a temperature of 372° C. and a load of 5 kg.

(Average Cell Size)

The average cell size was determined by taking a SEM image of the cross section of the electric wire, processing the image and calculating the diameters of the cells, and calculating the average value thereof.

(Capacitance)

The capacitance was determined using CAPAC300 19C (ZUMBACH Electronic AG).

(Number of Sparks)

The number of sparks per 3500 m was determined using Beta LaserMike Sparktester HFS1220 at a voltage of 1500 V.

(Expansion Ratio)

The expansion ratio was determined by $\{[(\text{specific gravity of fluororesin}) - (\text{specific gravity of foam})] / (\text{specific gravity of fluororesin})\} \times 100$.

Examples 1 to 23 and Comparative Examples 1 to

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Non-pulverized boron nitride (hereinafter, referred to as BN) powders having an average particle size of 22 μ m, 19 μ m, 15 μ m, 13.5 μ m, 13 μ m, or 8 μ m were prepared.

Non-pulverized BN powders having an average particle size of 19 μ m or 22 μ m were pulverized using a jet mill, preparing pulverized BN powders having an average particle size of 8.5 μ m, 13.5 μ m, or 14.5 μ m.

The particle size distributions of these non-pulverized BN powders and pulverized BN powders were determined. The particle size distributions of the BN powders in the respective examples and comparative examples are shown in Tables 1 to 4.

The non-pulverized BN powder or the pulverized BN powder was mixed with the following fluorinated FEP pellet such that the amount of the BN was 5% by weight of the sum of the amounts of the FEP pellet and the BN, and then a pellet was produced in the same manner as disclosed in WO 03/000792.

One of these pellets and one of the following fluorinated FEP pellets were melt-kneaded such that the amount of BN was as shown in one of Tables 1 to 4, thereby providing the target pellet (composition).

FEP pellet (A): produced by the same method as disclosed in JP 2011-514407 T (Example 2), TFE/HFP/PAVE copolymer, TFE/HFP/PAVE=87.5/11.5/1.0 (weight ratio), melting point: 255° C., melt flow rate (MFR): 23 g/10 min, total number of unstable end groups and —CF₂H end groups: 0

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FEP pellet (B): produced by the same method as disclosed in JP 2011-514407 T (Example 8), TFE/HFP/PAVE copolymer, TFE/HFP/PAVE=87.7/11.3/1.0 (weight ratio), melting point: 255° C., melt flow rate (MFR): 36 g/10 min, total number of unstable end groups and —CF₂H end groups: 0

FEP pellet (C): produced by the same method as disclosed in JP 2010-539252 T (Example 1), TFE/HFP/PAVE copolymer, TFE/HFP/PAVE=87.8/11.2/1.0 (weight ratio), melting point: 255° C., melt flow rate (MFR): 35 g/10 min, total number of unstable end groups and —CF₂H end groups: 0

FEP pellet (D): produced by the same method as disclosed in JP 2011-514407 T (Example 8) except that the amount of methanol for molecular weight adjustment was 125 LBS, TFE/HFP/PAVE copolymer, TFE/HFP/PAVE=87.7/11.3/1.0 (weight ratio), melting point: 255° C., melt flow rate (MFR): 41 g/10 min, total number of unstable end groups and —CF₂H end groups: 0

An extruder for foam molding was set to the extruder temperature shown in Table 6, and nitrogen gas as a foaming

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agent was introduced into the melt-kneading part of the extruder. The pellet (composition) produced by the aforementioned method was charged into the extruder for foam molding and then extrusion foam molded. The molded foam was then applied to the surface of a copper wire. Thereby, an electric wire comprising a covering material was produced. FIG. 1 is a photograph showing the cross section of the electric wire produced in Example 10.

The results of evaluating the properties of the resulting electric wires are shown in Tables 1 to 4.

The extruder for foam molding comprises an extruder and a system (each available from Hijiri Manufacturing Ltd.), a gas injection nozzle (Micodia), and a crosshead (UNITEK JAPAN Co., Ltd.). The structure and the conditions of the extruder are as shown in Table 5, and the screw comprises a mixing zone for uniformly dispersing the nitrogen introduced.

TABLE 1

		Comparative							
	Unit	Example 1	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
FEP	—	A	A	A	A	A	A	B	C
BN pulverization	—	Non-pul- verized	Non-pul- verized	Non-pul- verized	Non-pul- verized	Non-pul- verized	Pul- verized	Pul- verized	Non-pul- verized
Non-pulverized BN particle size	μm	8	13.5	15	19	22	19	19	13.5
Pulverized BN particle size	μm	—	—	—	—	—	8.5	8.5	—
Particle size distribution (D84 – D16)/D50	—	1.36	1.41	1.38	1.30	1.22	0.85	0.85	1.41
BN content	% by weight	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Nitrogen gas pressure in extrusion foam molding	MPa	30	30	30	30	30	30	30	30
Extrusion speed in extrusion foam molding	m/min	73	77	74.5	75	76.5	75	75.5	78
Number of sparks	/3500 m	0	2	1	20	19	0	0	0
Capacitance	pF/m	153	149	150	148	145	150	149	147
Expansion ratio	%	34	31	35	35	35	35	36	33
Average cell size	μm	38	31	29	25	37	31	31	31

TABLE 2

		Comparative				
	Unit	Example 2	Example 8	Example 9	Example 10	Example 11
FEP	—	A	A	A	A	A
BN pulverization	—	Non-pul- verized	Non-pul- verized	Non-pul- verized	Non-pul- verized	Non-pul- verized
Non-pulverized BN particle size	μm	8	13	15	19	22
Pulverized BN particle size	μm	—	—	—	—	—
Particle size distribution (D84 – D16)/D50	—	1.36	1.41	1.38	1.30	1.22
BN content	% by weight	0.6	0.6	0.6	0.6	0.6
Nitrogen gas pressure in extrusion foam molding	MPa	30	30	30	30	30
Extrusion speed in extrusion foam molding	m/min	70	75	73	74	74
Number of sparks	/3500 m	0	0	1	3	10
Capacitance	pF/m	156	146	150	149	151
Expansion ratio	%	30	35	34	33	36
Average cell size	μm	50	40	33	31	42

TABLE 3

	Unit	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19
FEP	—	A	A	A	A	B	B	C	D
BN pulverization	—	Pul-verized	Pul-verized	Pul-verized	Non-pul-verized	Pul-verized	Non-pul-verized	Pul-verized	Pul-verized
Non-pulverized BN particle size	μm	19	22	19	13.5	19	13.5	22	22
Pulverized BN particle size	μm	13.5	13.5	14.5	—	13.5	—	14.5	14.5
Particle size distribution (D84 – D16)/D50	—	0.92	0.86	0.97	0.93	0.92	0.93	0.97	0.97
BN content	% by weight	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Nitrogen gas pressure in extrusion	MPa	30	30	30	30	30	30	30	30
foam molding									
Extrusion speed in extrusion	m/min	75	75	75	75	75	76	76	76
foam molding									
Number of sparks	/3500 m	0	0	0	1	0	0	0	0
Capacitance	pF/m	148	149	150	147	146	146	148	148
Expansion ratio	%	35	36	34	34	36	35	36	36
Average cell size	μm	32	29	31	35	32	35	31	31

TABLE 4

	Unit	Comparative Example 3	Example 20	Example 21	Example 22	Example 23
FEP	—	A	A	A	A	A
BN pulverization	—	Non-pul-verized	Non-pul-verized	Non-pul-verized	Non-pul-verized	Pul-verized
Non-pulverized BN particle size	μm	8	13.5	19	22	19
Pulverized BN particle size	μm	—	—	—	—	13.5
Particle size distribution (D84 – D16)/D50	—	1.36	1.41	1.30	1.22	0.92
BN content	% by weight	0.4	0.4	0.4	0.4	0.4
Nitrogen gas pressure in extrusion	MPa	30	30	30	30	30
foam molding						
Extrusion speed in extrusion	m/min	68	72	72	72	71.5
foam molding						
Number of sparks	/3500 m	0	0	1	0	0
Capacitance	pF/m	155	152	151	151	149
Expansion ratio	%	28	33	33	33	32
Average cell size	μm	53	43	36	34	33

TABLE 5

Extruder conditions	
Extruder size	φ35 mm
Die size	4.7 mm
Tip size	2.2 mm
Screw revolution	18 rpm
Core (mm)	0.6 mm
Outer diameter (mm)	1.1 mm
Nitrogen pressure (MPa)	30 MPa
Nitrogen flow rate (cc/min)	Approximately 15 cc/min

TABLE 6-continued

Extruder temperature	
C4	380° C.
C5	380° C.
H1	375° C.
H2	365° C.
H3	360° C.

TABLE 6

Extruder temperature	
C1	330° C.
C2	360° C.
C3	370° C.

INDUSTRIAL APPLICABILITY

Since the compositions of the present invention each satisfy the aforementioned structures, they can provide covering materials having fine, uniform cells, and can suitably be used as a material for forming covering materials of foamed electric wires.

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The invention claimed is:

1. A composition comprising:
a fluoro-resin; and
boron nitride having an average particle size of 13.0 μm or greater,
wherein the amount of the boron nitride based on the sum of the amounts of the fluoro-resin and the boron nitride is 2.0% by mass or less,
wherein the fluoro-resin is one that has been subjected to fluorination so as to reduce unstable end groups.
2. The composition according to claim 1,
wherein the boron nitride has a particle size distribution represented by (D84–D16)/D50 of 1.2 or lower.
3. The composition according to claim 1,
wherein the boron nitride is in a pulverized form.
4. The composition according to claim 1,
wherein the fluoro-resin is a tetrafluoroethylene/hexafluoropropylene copolymer, a tetrafluoroethylene/perfluoro(alkyl vinyl ether) copolymer, or a tetrafluoroethylene/ethylene copolymer.
5. The composition according to claim 1,
wherein the amount of the boron nitride is 0.5% to 2.0% by mass based on the sum of the amounts of the fluoro-resin and the boron nitride.
6. A molded foam, which is formed from the composition according to claim 1.
7. An electric wire comprising
a core, and
a covering material which covers the core and which is formed from the composition according to claim 1.
8. A method for producing a molded foam, comprising foam-molding the composition according to claim 1.
9. A method for producing an electric wire, comprising covering a core with the composition according to claim 1, to provide an electric wire.
10. A composition comprising:
a fluoro-resin; and
boron nitride having a particle size distribution represented by (D84–D16)/D50 of 1.1 or lower.

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11. The composition according to claim 10,
wherein the boron nitride has an average particle size of 5.0 μm or greater.
12. A composition comprising:
a fluoro-resin;
boron nitride having an average particle size of 13.0 μm or greater, and a sulfonic acid or a salt thereof,
wherein the amount of the boron nitride based on the sum of the amounts of the fluoro-resin and the boron nitride is 2.0% by mass or less.
13. The composition according to claim 12,
wherein the boron nitride is in a pulverized form.
14. The composition according to claim 12,
wherein the fluoro-resin is a tetrafluoroethylene/hexafluoropropylene copolymer, a tetrafluoroethylene/perfluoro(alkyl vinyl ether) copolymer, or a tetrafluoroethylene/ethylene copolymer.
15. The composition according to claim 12,
wherein the amount of the boron nitride is 0.5% to 2.0% by mass based on the sum of the amounts of the fluoro-resin and the boron nitride.
16. The composition according to claim 12,
wherein the sulfonic acid or a salt thereof is a sulfonic acid represented by the following formula (1):
$$\text{F}(\text{CF}_2)_n\text{SO}_3\text{H} \quad (1)$$

wherein n is 4 or 5, or the following formula (2):
$$\text{F}(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{SO}_3\text{H} \quad (2)$$

wherein n is 4 or 5, or a salt thereof.
17. A molded foam, which is formed from the composition according to claim 12.
18. An electric wire comprising
a core, and
a covering material which covers the core and which is formed from the composition according to claim 12.
19. A method for producing a molded foam, comprising foam-molding the composition according to claim 12.
20. A method for producing an electric wire, comprising covering a core with the composition according to claim 12 to provide an electric wire.

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